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Comparison of CDI and MCDI applied with sulfonated and aminated polysulfone polymers

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Abstract. In this study, polysufone (PSf) was used as a base polymer to synthesize sulfonated polysulfone (SPSf) and aminated polysulfone (APSf) as cation and anion exchange polymers, respectively. Then the ion exchange polymers were coated onto the surface of commercial carbon electrodes. To compare the capacitive deionization (CDI) and membrane capacitive deionization (MCDI) processes, the pristine carbon electrodes and ionic polymer coated electrodes were tested under various operating conditions such as feed flow rate, adsorption time at fixed desorption time, and feed concentration, etc., in terms of effluent concentration and salt removal efficiency. The MCDI was confirmed to be superior to the CDI process. The performance of MCDI was 2-3 times higher than that of CDI. In particular, the reverse desorption potential was a lot better than zero potential. Typically, the salt removal efficiency 100% for 100 mg/L NaCl was obtained for MCDI at feed flow rate of 15 ml/min and adsorption/desorption time of 3 min/1 min and applied voltages 1.0 V for adsorption and -0.3 V for desorption process, and for 500 mg/L, the salt removal efficiency 91% was observed.

Keywords: sulfonated polysulfone (SPSf); aminated polysulfone (APSf); capacitive deionization (CDI); membrane capacitive deionization (MCDI); salt removal efficiency; effluent concentration

1. Introduction

CDI (capacitive deionization) is one of the desalination processes to remove ions in solution by using the principle of adsorption/desorption in electrical double layers at the interface between electrodes and electrolyte solution (Xu *et al*. 2008, Ryoo *et al*. 2003, Welgemoed and Schutte 2005, Baek *et al*. 2008, Suss *et al*. 2015). When electric potentials run through two electrodes, cations and anions in a brine running between electrodes are adsorbed in the cathode and anode, respectively. Once the electrode surface is saturated with ions, it is possible to restore electrodes by desorbing ions on the electrode surface by the repulsive force as the electric potentials applied to electrodes turn to be 0V or as electric potentials are reversely applied. Electrodes used in the CDI process are porous carbon electrodes. Basic requirements include the large surface area depending on the pore volume and size, high electric conductivity, stability despite environmental changes, tolerance to organic pollutants and scale formation, and so forth (Lee *et al*. 2009). There are different types such as active carbon powder, active carbon fiber, carbon nanotube, carbon aerogel,

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Table 1 Energy requirement comparison for RO and CDI desalination technology (Oren 2008)

Desalination technology	Energy consumption	Remark
RO	3.5~4.0 kWh/m^3	Seawater
	1.0~1.4 kWh/m^3	1,000~4,000 ppm
CDI	0.3~0.8 kWh/m^3	1,000~4,000 ppm

graphene, etc. (Choi 2014). Since the CDI process is operated in an electric potential area where electrical double layers are formed, electrochemical oxidation or deoxidization hardly takes place. Hence, this desalination technology consumes a low level of energy, and the manipulation is easy since ion adsorption/desorption and repeated operation are possible based on potential difference of electrodes. In addition, since no additional chemicals are used in the reproduction process, it is eco-friendly with high rates of recovery (Lim *et al*. 2009). Owing to these advantages, this is widely used for ultrapure water preparation, heavy metal recovery, hardness material removal, desalination process, etc. (Lee *et al*. 2005). Table 1 compares energy consumption of reverse osmosis membranes, which are most commonly used in desalination processes, and that of the CDI process. Within the range of density to which the CDI process is applicable, the level of energy consumption is lower than that of reverse osmosis membranes. Zhao *et al*. (2013a) carried out the comparison research for the energy consumption of membrane capacitive deionization (MCDI) with reverse osmosis (RO) and concluded that MCDI was more energy efficient for feed water with salinity lower than 60 mM, to obtain freshwater of ~1 g TDS/L.

However, in the process of ion adsorption with electric potentials running on electrodes and desorption with approved electric potentials discharged, not all the adsorbed ions are desorbed, but remain on the interface of electrodes. The following adsorption process then involves re-adsorption of remaining ions, which deteriorates the desalination efficiency (Jung *et al*. 2007). To solve this problem, introduced was the membrane capacitive deionization (MCDI) technology that combines electrodes and ion exchange membranes (Kim and Choi 2009, Biesheuvel and van der Wal 2010). While existing processes combine commercial ion exchange membranes on the electrode surface, this new process adopts the concept of complex carbon electrodes which reduce electrodes and contact resistance by enhancing the ion selectivity instead of using ion exchange membranes. With the electrode surface coated with ion exchange polymers, the structure of electrodes is simple and the cell structuring is easy. In addition, it is possible to reduce contact resistance between the existing membrane and electrodes. With electric potentials running, the contact with carbon and inflows, which may act as an electric catalyst to carbon electrodes, is prevented, and this helps controlling electrode reactions (Kim and Choi 2010b, Lee *et al*. 2010). Park *et al*. (2007) applied the MCDI process to desalination of power plant waste water and reported that as a result, salt removal rates were 19% improved than those of the CDI process. Li *et al*. (2002) combined carbon nanotubes and nanofiber selectrodes with ion exchange membranes in the MCDI process and demonstrated that salt removal rates of the MCDI process were 49% higher than those of the CDI process. Also to enhance the performance of CDI, identification of electronic and ionic resistances in the CDI cell was investigated (Biesheuvel *et al*. 2016). They found that that for inflow salt concentrations of 20 mM the resistance is mainly located in the spacer channel and the external electrical circuit, not in the electrodes. Based on these findings, the carbon electrode thickness could be increased without significantly increasing the energy consumption per mol salt removed.

For this study, polysulfone (PSf) was synthesized into cation exchange polymers and anion exchange polymers through sulfonation and amination, respectively. Commercially available porous carbon electrodes of Pureechem Co. were purchased and applied to the CDI process, and the aminated and sulfonated PSf synthesized in our lab was coated on the surface to produce complex carbon electrodes. To compare the performance of the MCDI process under the same conditions, the effluent concentration and salt removal efficiency were measured. In the CDI and MCDI processes for unit cells with NaCl solution as feed water, operation conditions such as adsorption time, feed flow rates, and feed concentration were changed. Such factors as effluent concentration, desalination efficiency, etc. were comparatively examined.

2. Experimental

2.1 Materials

Udel® PSf was obtained from Solvay Plastics. Chloroform, methanol, dichloroethane (DCE), tin chloride ($SnCl_2$), 1-Methyl-2-pyrrolidinone (NMP, 99.5%), and dimethyl acetamide (DMAc) were purchased from Sigma-Aldrich Co. (Milwaukee, USA). Chlorosulfonicacid (CSA), sodium chloride, chlorotrimethylsilane (TMCS) and trimethylamine (TMA) were purchased from Junsei Co., Japan. And chloromethyl ethyl ether (CMEE) was provided from Kanto, Japan. All reagents and solvents were used without further purification. The carbon electrodes were provided from Pureechem Co. (Cheongwon, Chungbuk, Korea).

2.2 Ion exchange polymer synthesis

2.2.1 Cation exchange polymer

With 10 g of PSf dissolved in 100 ml of DCE, CSA and TMCS are mixed at the molar ratio of 1:1 for sulfonation, which is followed by stirring for at least 5 hours. After the sulfonation agent relative to the monomer molar ratio was added into the PSf solution, reaction was progressed for 8 hours. After the sulfonation reaction, MeOH is added, which is followed by stirring for at least 24 hours. Cleaning solution is then prepared with de-ionized water and MeOH mixed at the volume ratio of 1:1. And cleaning is conducted for at least 24 hours. Once the cleaning process is completed, resulting polymer were sliced, dried at 60℃ for at least 24 hours, and dried again by means of a vacuum drier for 3 days (Shin *et al*. 2002). The resulting sulfonated PSf (SPSf) was stored in a desiccator under a nitrogen purged gas environment.

2.2.2 Anion exchange polymer

Aminated polysulfone (APSf) is produced through the 2-step reaction: (1) Under the existence of $SnCl_2$, a Friedel-Crafts catalyst, the chloromethylation reaction between PSf and CMEE is progressed; and then (2) amination reaction of chloromethylated PSf is facilitated by the addition of TMA (Komkova *et al*. 2004). In detail, the chloromethylation of PSf was carried out by dissolving PSf in dichloroethane while stirring to form an 8 wt% solution. Then the catalyst, $SnCl_2$, was added at 10 wt% of the PSf and an amount of chloromethyl ethyl ether 4 times that of the PSf was introduced very slowly followed by stirring at 40℃ for 4 h. After the reaction, the solution was washed with methanol several times and dried at 60℃ for 24 h in a forced convection oven. Next, the desired molar ratio of TMA against CMEE was added into the chloromethylated PSf dissolved in DMAc and kept for more than 12 h at room temperature to synthesize aminated PSf

(APSf). The resulting APSf was stored in a desiccator under a nitrogen purged gas environment.

2.3 Characterization of synthesized polymers and preparation of composite carbon electrodes

To characterize the electric and physical properties of synthesized SPSf and APSf, the swelling degree, ion exchange capacity, and ion conductivity were measured. For the measuring method, consult the references (Kim *et al*. 2015a, b). And to prepare the composite carbon electrodes, the synthesized solutions were cast onto the carbon electrodes provided by Pureechem Co. (Cheongwon, Chungbuk, Korea) mentioned above and dried at 80℃ in a forced convection oven for several hours. The effective electrode size was 10 cm × 10 cm. The resulting electrodes were stored in deionized water until use.

2.4 Scanning electron microscope (*SEM*)

To check if the electrode surface was coated properly with ion exchange polymer solution, SEM pictures of FE-S-4800 (Hitachi, Japan) were observed. Prior to the analysis, electrodes were completely dried in a vacuum oven, and samples were collected by means of liquid nitrogen to prevent the sectional structure from being destroyed. Samples were then fixed on a metallic plate and prepared to be coated with Pt.

2.5 CDI experiment

Fig. 1 shows the diagram of the process used in this experiment. There was no difference between the CDI and MCDI processes except for the coating of ion exchange polymers on the electrode surface, i.e., the electrode surface at the positive potential side was coated with APSf, anion exchange polymer while that of the negative potential side was coated with SPSf, cation exchange polymers. The effective area of electrodes was 10 × 10 cm^2. A spacer (nylon) with about 100 μm thickness was inserted between two electrodes to prevent electrodes from being in contact with each other and to secure space of feed flow. NaCl feed solution was supplied at the fixed flow rate by means of a peristaltic pump. Feed water was provided through the two holes at the cell edge and was discharged from the hole in the middle. Potential difference was adjusted by means of potentiostat (WonATech Co. WPG 100). Solution that came out through the outlet in the middle was measured at every 3 seconds by means of TDS conductivity meter (iSTEK, EC-470L), and the data was saved in the computer in real time. First, to find the effect of adsorption time, NaCl 100 mg/L feed solution was flowed in, and an experiment was conducted where the adsorption time was set to 2, 3, 5, and 7 minutes with the adsorption/desorption electric potential set to 1 V and 0 V, respectively. Second, the flow rates were set to 15, 25, and 30 ml/min with 100 mg/L of NaCl feed solution and adsorption/desorption set to 1 V/0V. Third, the concentration of NaCl feed water was increased from 100 to 500 mg/L at the intervals of 100 with the adsorption/desorption set to 1 V/-0.3 V. Salt removal efficiency may be calculated as in Eq. (1) (Biesheuvel *et al*. 2009).

$$\text{Salt removal efficiency (\%)} = \left(1 - \frac{C_{eff}}{C_0}\right) \times 100 \qquad (1)$$

where C_0 and C_{eff} indicate the concentrations of feed and effluent, respectively.

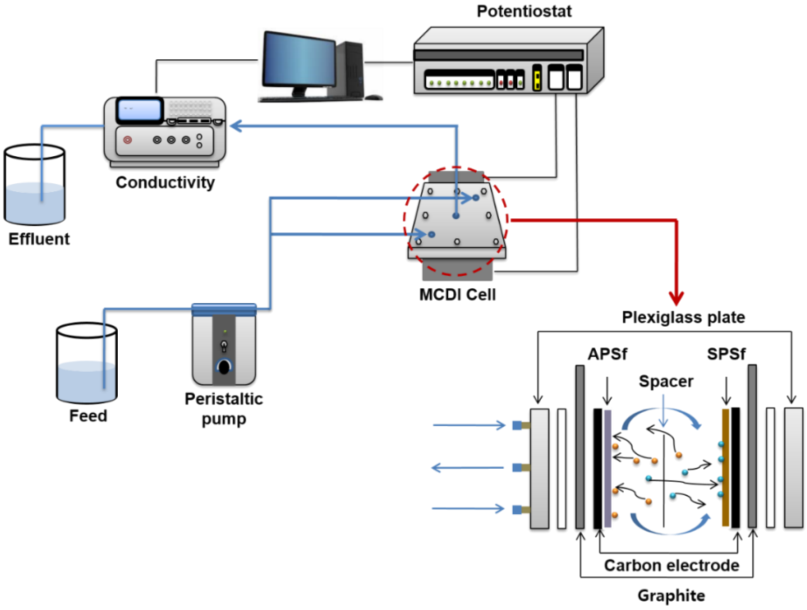


Fig. 1 Schematic diagram of experimental apparatus and MCDI cell configuration

Table 2 Basic properties of the synthesized ion exchange polymer for MCDI application

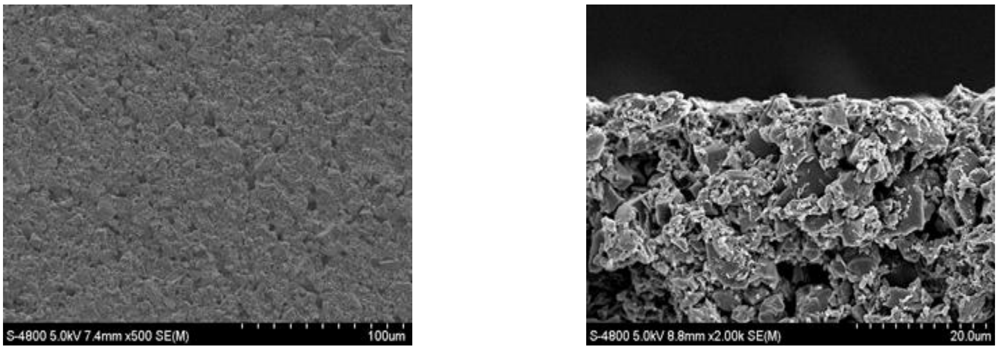
	Swelling degree (%)	Ion exchange capacity (meq/g)	Ion conductivity (S/cm)
APSf	14.4	2.61	0.027
SPSf	21.6	2.20	0.106

3. Results and discussion

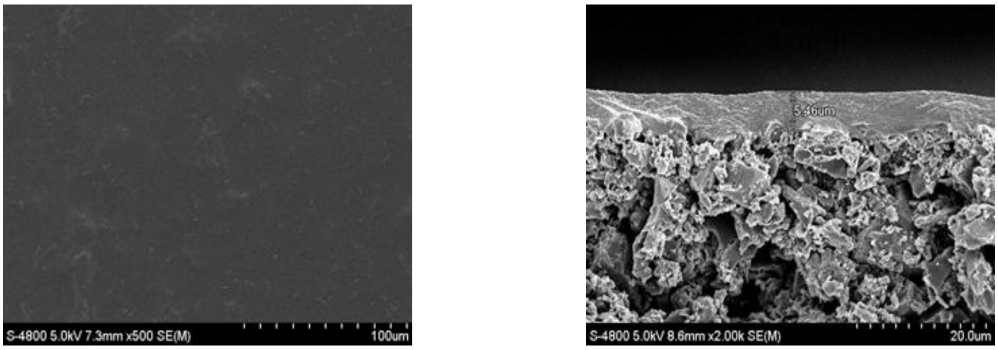
The separation performance of MCDI may be dependent on the number of exchange sites in the ion exchange polymers. Also the ion exchange membrane is known to be very hydrophilic because of hydrophilic ionic groups such as –SO$_3^-$, -COO$^-$, and -PO$_3^{2-}$atthecation exchange membrane (CEM) and –NH$_3^+$, -NRH$_2^+$, -NR$_2$H$^+$, -NR$_3^+$, and -PR$_3^+$at the anion exchange membrane (AEM) (Xu 2005). These hydrophilic functional groups stimulate dimensional changes in the ion exchange membranes so that the intra-molecular spaces become wide enough for ions to pass into the membrane more freely at a certain desired adsorption time depending on the ion exchange capacity values. Typical basic properties of the synthesized ion polymers used for MCDI are shown in Table 2.

3.1 Scanning Electron Microscope (*SEM*)

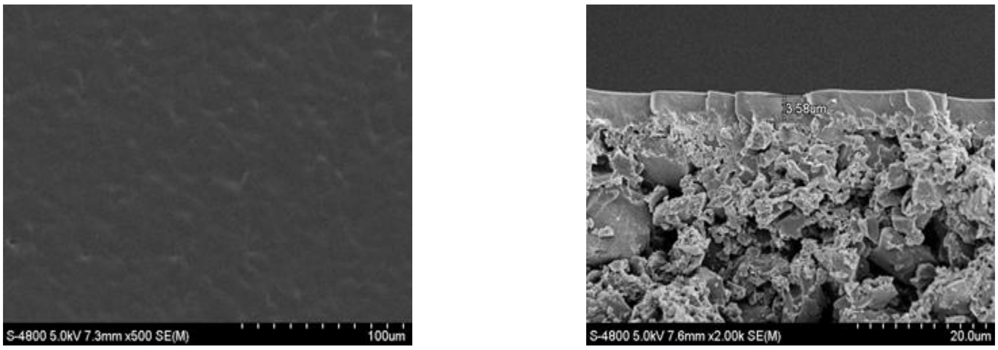
If the surface layers of porous carbon electrodes coated with ion exchange polymers were coated properly, SEM images of the surfaces and cross-sections of the plain electrode and ion exchange polymer-coated electrodes were taken (Fig. 2). Prior coating, active carbon particles on the electrode surface were exposed while an even coating layer of ion exchange polymer after coating was formed onto the carbon particle layer. Both the surface and cross-section were



(a) Pristine carbon electrode



(b) SPSf coated electrode



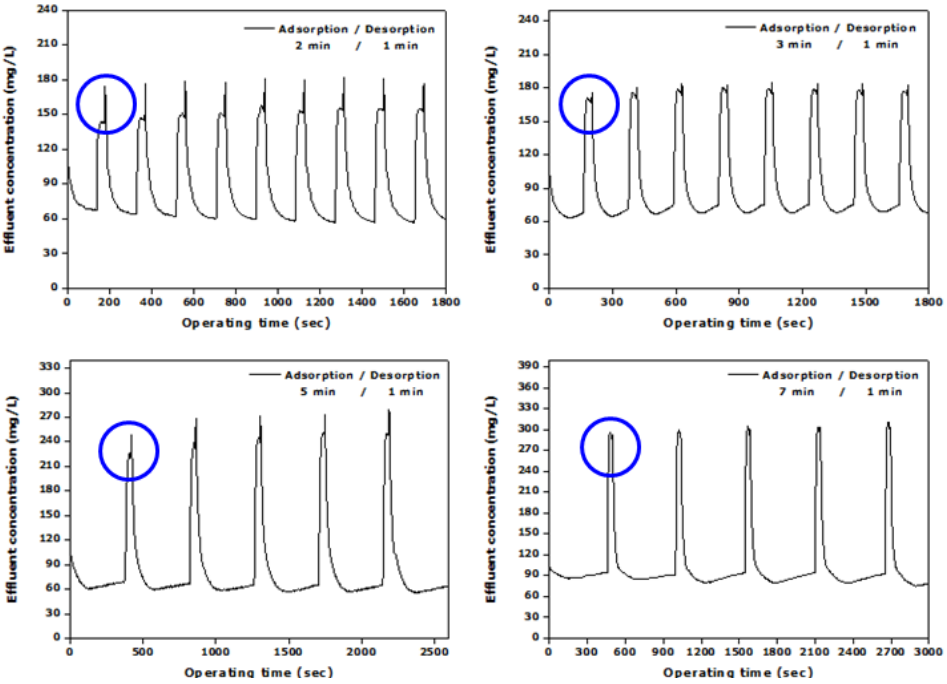
(c) APSf coated electrode

Fig. 2 SEM images of surface (left-hand side) and cross-section (right-hand side) of (a) pristine carbon electrode; (b) SPSf coated electrode and (c) APSf coated electrode

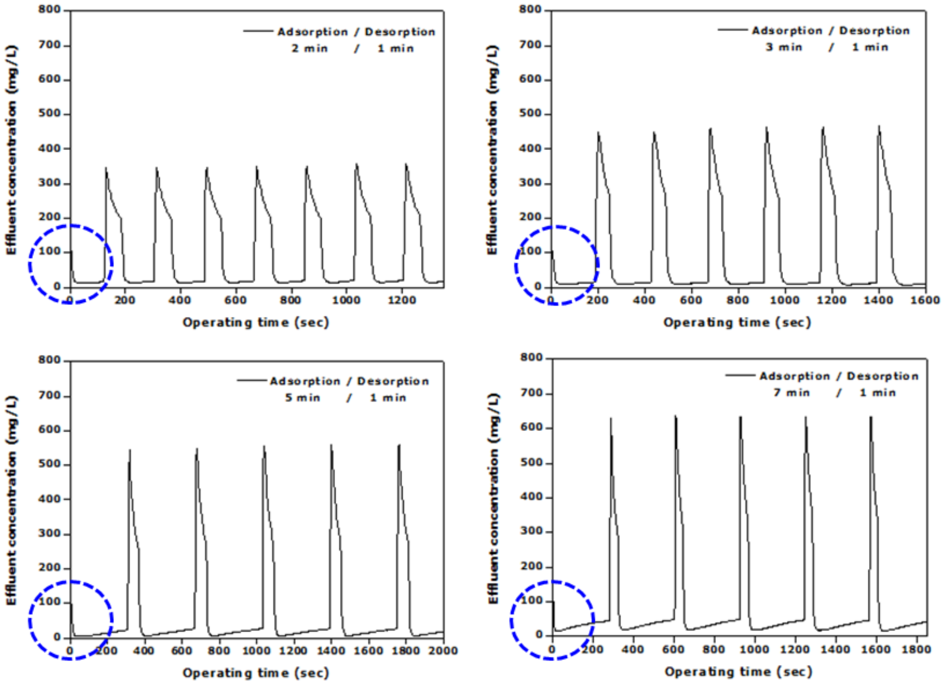
smoothened after coating as seen in (b) and (c). The thickness of the coating layer of cation exchange polymer was about 5.46 μm while that of anion exchange polymer was 3.58 μm.

3.2 Effect of adsorption/desorptiontime

To compare the performance of existing porous carbon electrode with that of complex carbon electrode coated with ion exchange polymer, they were applied to unit cells and then electric potentials applied. While adsorption/desorption time was adjusted, the effluent concentrations



(a) CDI process



(b) MCDI process

Fig. 3 Effect of adsorption time on effluent concentration at the fixed desorption time of 1 min, feed flow rate of 25 mL/min, NaCl 100 mg/L feed concentration, and adsorption/desorption potential of 1.0 V/0 V for (a) CDI; and (b) MCDI process

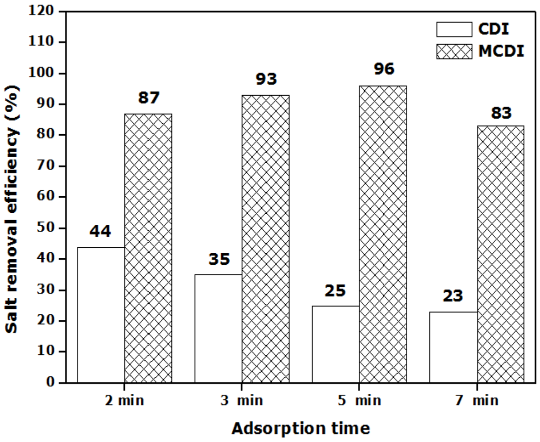


Fig. 4 Salt removal efficiency in accordance with adsorption time for CDI and MCDI at the same conditions mentioned in Fig. 3

were measured. The result is presented in Fig. 3. In the case of CDI, as the adsorption time increased from 2 min. to 7 min, the effluent concentration increased from 182 to 289 ppm gradually. The minimum value increased from 62 to 82 ppm, which is probably because the adsorption rate decreased as the adsorption continued on the electrode surface gradually over time. Another peak is seen in the desorption period (Fig. 3(a) the solid line circle): In the adsorption process, ions of opposite electrical charges on the electrode surface became adsorbed while ions of the same charges were pushed out, which resulted in the increase of effluent concentration (Li *et al*. 2012, Li and Zou 2011). In the case of MCDI, whose operation condition was the same with that of CDI, a steep inclination is observed in the first adsorption period (Fig. 3(a) the dotted line circle). Unlike the case of CDI, ion exchange membranes were in direct contact with feed water, and thus adsorbed ions at anode and cathode were desorbed and the ions moved toward the counter electrodes. Adsorption was prevented due to the cation/anion exchange membrane on the surface of counter electrodes. As a result, the adsorption time increased from 2 to 5 minutes, which decreased the minimum value down to 13, 7, and 4 mg/L. However, when the adsorption time was 7 minutes, the minimum value was 17 mg/L, which is larger than values of other adsorption time. It may be considered that the adsorption rate was slowed down after the limitation of adsorbed capability of electrodes. Thus, it is found that a longer adsorption time always leads to the better result, but 5 minutes would be most appropriate for the present system. In contrast, the maximum concentration at the discharge period was 348 mg/L at 2 minutes and then increased up to 635 mg/L at 7 minutes. This result indicates that with ion exchange polymers coated, the movement of counter electrical charges is changed due to the selectivity of the membrane, which leads to a fast response in the adsorption period and an increase of the adsorption volume. The existence of ion exchange membranes, therefore, helps the adsorption process, and the adverse effects indicated with the two circles in Fig. 3(a) can be removed.

Next Fig. 4 shows the salt removal efficiency of CDI and MCDI calculated by Eq. (1). In the case of CDI, the removal rate continued to decrease from 44% at 2 minutes to 23% at 7 minutes. As for the removal rate in the case of MCDI, the efficiency at 2 minutes where the adsorption time was relatively short, was almost double. As the adsorption time increased, the rate increased up to 96% at 5 minutes, which is almost 4 times to that of CDI. At minutes, however, the minimum

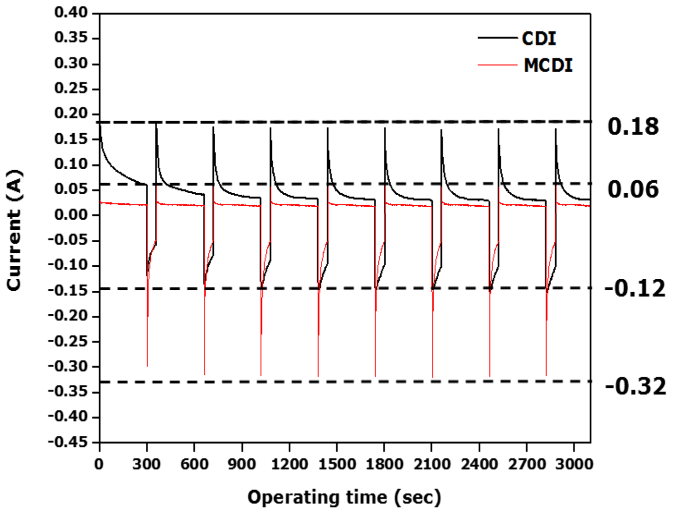
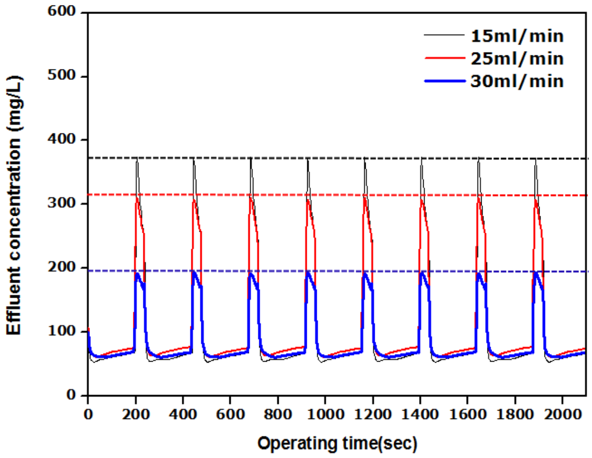


Fig. 5 Current response for 5 min adsorption/1 min desorption time in CDI and MCDI processes at a potential of 1.0 V, feed concentration of 100 mg/L NaCl and flow rate of 25 mL/min

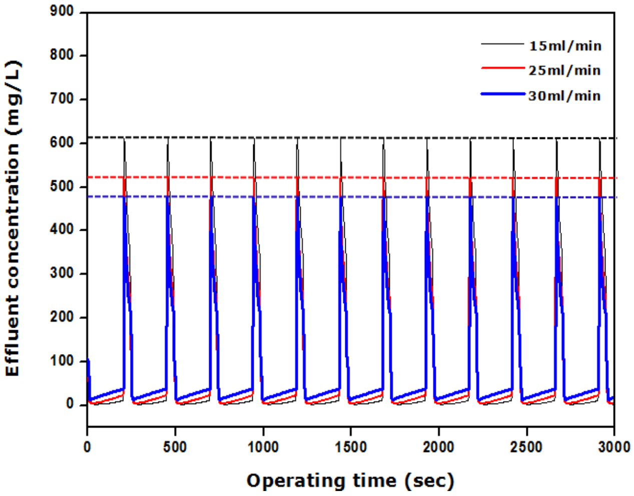
value of effluent concentration became higher than that of the shorter adsorption time, which decreased the salt removal efficiency down to 83%.In the case of CDI, as the salt removal rate gradually decreased, counter-ions became adsorbed on the electrode surface because of the voltage applied to electrodes. In desorption thereafter, ions remained on the electrode, not being completely desorbed. Remaining ions on the electrode surface induced counter-ions to maintain electric neutrality. If potential was applied again, the same vicious cycle would be repeated up to the point of deteriorating the salt removal efficiency. To solve this problem, the MCDI process is introduced. As the adsorption time increases in CDI, this phenomenon is more highly probably, and thus it may be advantageous to operate in the range of short adsorption time.

3.2.1 Current

With the adsorption/desorption time set to 5/1 minute respectively, the current flow in CDI was compared with that in MCDI, and the result is presented in Fig. 5. As shown in the figure, all the cycles are stabilized and reproducible. In the adsorption period, the steep decrease of current was observed both in CDI and MCDI, and that in MCDI was steeper. In particular, the decrease from 0.06 A to 0.025 A was quite drastic for MCDI while the decrease for CDI was just from 0.18 A to 0.04 A. Current flow is used as a means to examine ion mobility mechanisms in electrodes. When voltage is applied to electrodes repeatedly, ions in an electrical double layer are divided into two at both sides of electrodes, and at the same time, they are moved toward to the bulk. As a result, high current is required to move ions in the initial step of adsorption for CDI (Li and Zou 2011).The desorption rate may be determined in indirect connection with current change. As shown in Fig. 5, the patterns of current change in the two processes are distinctively different from each other. First of all, current in CDI and MCDI decreased down to -0.12 A and -0.32 A repeatedly, and then increased up to -0.08 A and -0.04 A. That of MCDI was higher than that of CDI because ion exchange membranes effectively blocked co-ions, which lowered electric resistance and facilitated ionic migration from the bulk solution toward the boundary layer (Liang *et al*. 2013).



(a) CDI



(b) MCDI

Fig. 6 Effect of flow rates on effluent concentration for CDI and MCDI at adsorption/desorption time of 5 min/1 min, NaCl 100 mg/L feed concentration, and adsorption/desorption potential of 1.0 V/0 V

3.3 Feed flow rate

To examine the effect of feed flow rate change on adsorption/desorption characteristics, 100 mg/L NaCl of feed flow was supplied with the flow rate change from 10 to 25 and 30 ml/min. at the fixed adsorption/desorption of 1.0/0 V and its effect on effluent concentration was observed. For CDI in Fig. 6(a), the lower flow rate to a unit cell was provided, the higher concentration of effluents was observed. It may be considered that the residence time of supplied liquid is shorter when the flow rate is higher. Besides, when no voltage is applied, ions in the bulk area flow horizontally on the electrode surface, but once voltage is applied, ions move vertically toward the electrode. The number of ions heading for the electrodes would decrease as the flow rate increased, which decreases the effluent concentration accordingly. As the flow rate increased from 15 to 25

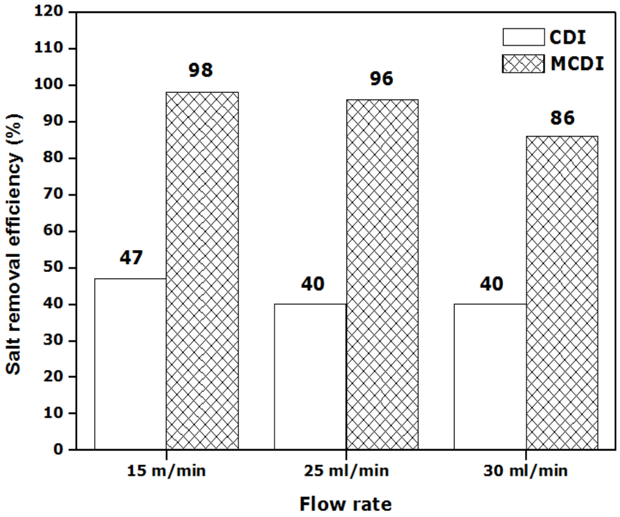


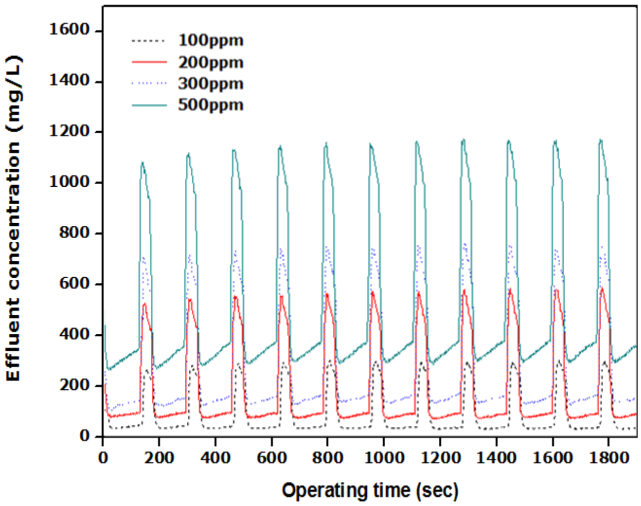
Fig. 7 Salt removal efficiency relative to feed flow rates for CDI and MCDI at the same conditions mentioned in Fig. 6

and to 30 ml/min, the effluent concentration decreased from 374 to 311 and to 192 mg/L. MCDI is a quite complicated, dynamic process that involves various operation conditions such as geometric details of the electrode structure, molecular reactions, physico-chemical properties of ion exchange membranes, feed flow rates, components in feed, flow channels, and so forth (Biesheuvel and van der Wal 2010). With regard to the relation between operation time, flow rates, and effluent concentration, Choi (2014) and Biesheuvel *et al.* (2009) demonstrated through a simple numerical analysis model that effluent concentration would increase in proportion to flow rates, which corresponds to the result of this experiment. A similar result was presented by Kim (2010). As flow rates increased in CDI, the effluent concentration in MCDI was 600, 510, and then 466 mg/L. The concentration in the adsorption period increased from 2 to 4 and to 14 mg/L as flow rates increased.

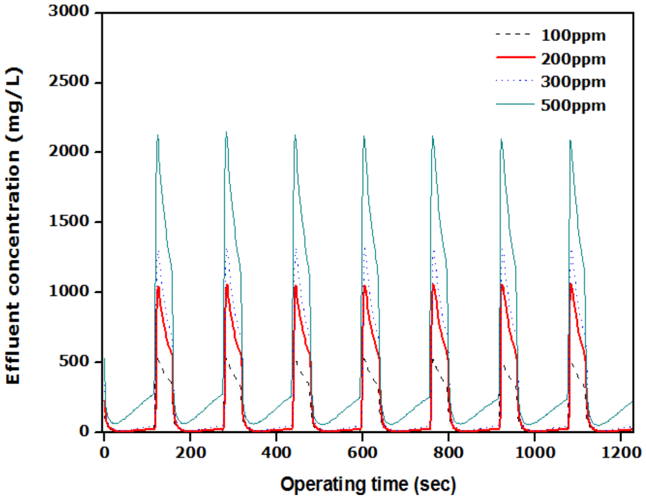
Salt removal efficiency of CDI and MCDI in relation to rate change was calculated by Eq. (1) and based on Fig. 6 above, and the result is presented in Fig. 7.

3.4 Feed concentration

As the feed concentration was adjusted to 100, 200, 300, and 500 mg/L, the effect was examined in terms of the effluent concentration (Fig. 8). At this stage, 3 minutes of the adsorption time with the potential of 1.0 V and 1 minute of desorption time with the potential of -0.4 V, and flow rates of 15 ml/min were used. When the feed concentration was low, the effluent concentration decreased accordingly due to the high resistance of the spacer and the fast exhaustion of ions (Biesheuvel 2009). As for CDI, when the feed concentration was 100 mg/L, the effluent concentration decreased down to 52 mg/L. As the concentration increased to 200, 300, and 500 mg/L, the minimum value increased to 75, 145, and 309 mg/L. On the other hand, as for MCDI, in the low concentration of 100 mg/L, the minimum value reached 0 and then gradually increased to 2, 4, and 9 mg/L. In contrast, the effluent concentration upon desorption for CDI increased from 308 mg/L to 1190 mg/L when the feed concentration was 500 mg/L. In the case of MCDI, the concentration increased from 511 up to 1950 mg/L at the same condition.



(a) CDI



(b) MCDI

Fig. 8 Effect of the feed concentration on the effluent concentration at feed flow rate of 15 ml/min and adsorption/desorption time of 3 min/1 min and applied voltages 1.0 V for adsorption and -0.3 V for desorption process, respectively

The salt removal efficiency of each process in relation to the feed concentration was calculated by Eq. (1) and depicted in Fig. 9. As the feed concentration increased, the salt removal efficiency of both processes decreased accordingly. As for CDI, the salt removal efficiency decreased from 48% to 32% while that of MCDI decreased from 100% to 91%. The efficiency was 100% for 100 mg/L feed, which is higher than 98% as shown in Fig. 7. It may be considered that 0 V of cell voltage in the previous case and -0.3 V of reverse voltage now are applied upon the desorption period in the operation condition. This also indicates that upon desorption, the efficiency would be improved if minus reverse voltage was applied rather than 0V.

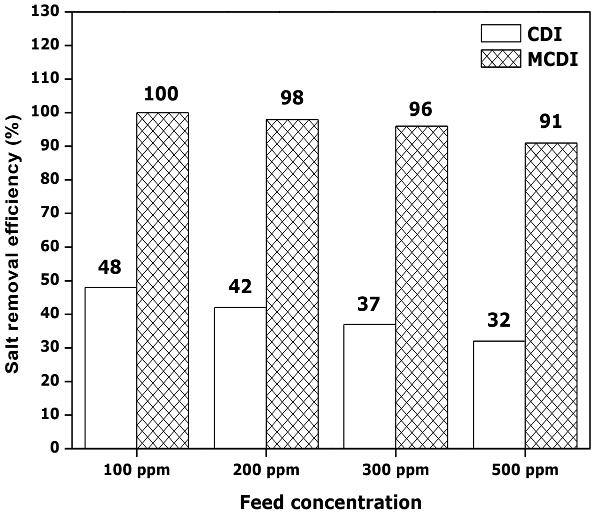


Fig. 9 Salt removal efficiency in accordance with feed concentration for CDI and MCDI at same conditions mentioned in Fig. 8

4. Conclusions

In this study, the sulfonated polysulfone (SPSf) and aminated polysulfone (APSf) as cation and anion exchange polymers, respectively, were synthesized. The synthesized ionic polymers were coated onto the surface of commercial carbon electrodes, then the performances of CDI and MCDI were compared in terms of effluent concentration and salt removal efficiency under the various operating conditions such as feed flow rate, adsorption time at fixed desorption time, and feed concentration, etc. From this study, several conclusions can be drawn as follows:

- As the adsorption time increases from 2 to 7 min, the salt removal efficiency for CDI tends to decrease whereas the removal efficiency increases from 2 to 5 min and then decreases at 7 min due to the over capability of the carbon electrode. For CDI, the best efficiency of 44% was obtained at the adsorption time, 2 min and for MCDI, 96% was observed at 5 min adsorption time.
- It was observed that introduction of both cation and anion exchange polymers was effective in preventing the “co-ion” effect. As a result, the current values at both adsorption and desorption stages for MCDI were much lower than for CDI.
- Both the effluent concentration during desorption and salt removal efficiency become higher with lowering feed flow rate for both processes. Typically, 47 and 98% of the salt removal efficiency for CDI and MCDI, respectively, were obtained.
- As the feed concentration increased, the salt removal efficiency was decreased for both CDI and MCDI. Typically, the salt removal efficiency 100% for 100 mg/L NaCl was obtained for MCDI and for 500 mg/L, the salt removal efficiency 91% was observed. In the meantime, 48% and 32% were obtained for 100 and 500 mg/L, respectively, for CDI.
- Finally, another conclusion is that the minus desorption potential was superior to zero voltage potential. The former case was observed 100% removal while the latter 98% obtained.

Acknowledgments

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